

DEVELOPMENT OF A THORIA FLOWSHEET
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INTRODUCTION

Over the past few years discussions have been held with the Chalk River Laboratories of AECL on the possibility of producing nuclear purity ThO_2 . Recently, CANMET and AECL entered into a joint-funded research program to develop a suitable process flowsheet for the production of thorium. The purpose is to establish a domestic source for nuclear purity thorium for future fueling of the breeder reactors. CANMET had previous experience on the treatment of Elliot Lake solutions for the removal and recovery of thorium (1,2), and with this background the present work was initiated. Ion exchange barren solutions from the uranium mills in Elliot Lake could be the feed solution.

Work had been reported in the past on Rio Algom's circuit in which they used an undisclosed organophosphorus extractant to recover the thorium from the barren solutions at pH 1.8(3). Thorium was stripped using strong (10 N) H_2SO_4 and the thorium sulphate subsequently crystallized. The product was repulped in 10 N H_2SO_4 to remove impurities and the crude $\text{Th}(\text{SO}_4)_2$ was suitable for feed material to subsequent refining.

Other work was reported on the use of DEHPA for treatment of the Elliot Lake barren solutions(4). Because ferric iron is extracted strongly, the feed solution was reduced with iron filings prior to solvent extraction of the thorium. Again the product was an impure $\text{Th}(\text{SO}_4)_2$ material which would require additional processing for high purity thorium.

The Oak Ridge National Laboratory reported on the use of amines for the extraction of thorium from such feed solutions(5), and subsequent research at CANMET was aimed at finding a solvent extraction process for the co-extraction of uranium and thorium from ion exchange barren solution or from leach solutions(2). The extractant selected for that work was the primary amine, Primene JMT (Rohm and Haas manufacturer), which showed the best combination of Th and U co-extraction with maximum iron rejection. If the proper phase ratio was provided for solvent solution with respect to thorium and uranium, no rare earths were extracted. The thorium was recovered by stripping either with 5% Na_2CO_3 solution or 5 to 10 vol % HNO_3 . The flowsheet as developed was primarily to produce UO_3 and a mill grade thorium sulphate product(2), and not high purity thorium. More recent work by the University of Sydney used Adogen 283, a secondary amine to recover thorium from a solution resulting from the decomposition

of monazite and the prior extraction of uranium⁽⁶⁾. The solvent was stripped with 1M $(\text{NH}_4)_2\text{CO}_3$ solution at pH 9-10, (adjusted with NH_4OH). Following stripping, the strip solution was adjusted with HCl to destroy the carbonate, and a thorium product was produced by oxalic acid precipitation, filtration and ignition to an oxide. This also contained some rare earths.

The results of the previous work thus indicated the possibility existed for the extraction of thorium but no high purity thoria resulted. The present program will attempt to produce a high purity thoria material, possibly through a 2 stage extraction system.

PROCEDURE

Bench-scale tests were performed in separatory funnels to determine the various parameters of extraction, scrubbing, stripping and re-extraction into a separate system. Because the primary amine, Primene JMT had proven of interest in previous CANMET investigations⁽²⁾, this reagent was used, realizing that if it did not perform sufficiently well with respect to the purity, then additional screening tests would be required. The Primene solvent was pre-equilibrated with 5% H_2SO_4 prior to contact with the leach liquor. Also in the second extraction circuit, it was considered that TBP might be a suitable reagent. Following the bench tests, continuous testing was on a small Bell Engineering countercurrent mixer settler apparatus.

The feed liquor was the ion exchange barren as supplied by Denison Mines Ltd. The 0.1 M. (4%) Primene JMT was dissolved in Varsol 140 containing 5% isodecanol as a modifier. Some extraction tests were also performed on synthetic solutions.

RESULTS

Extraction of Thorium from the Ion Exchange Barren Solution into Primene JMT

a) Equilibrium Curve and McCabe Thiele Plot

A series of bench tests, at varying phase ratios, was carried out on the as-received Denison ion exchange barren solution, using a 5 minute contact time. Prior to extraction, the 0.1 M Primene JMT was equilibrated with 5% H_2SO_4 , O/A 5/1. The feed solution contained, in g/L: 0.25 Th, 0.013 U, 2.75 Fe^{I} , 1.96 Fe^{2+} , and the pH was 2.15. The distribution, or

equilibrium curve is shown in Fig. 1, together with the McCabe-Thiele plot. The data suggest that one theoretical stage is required to extract from such a solution using 0.1 M solvent, in order to obtain a raffinate containing less than 0.002 g Th/L.

b) Kinetics of Extraction

Kinetic tests over a range of 10 seconds to 180 seconds indicated thorium extracts quickly, in less than 1 minute. About 30 seconds could provide for Th/Fe and Th/U ratios in the solvent of 170 and 240 respectively and these are the best values in the range studied.

c) Effect of Successive Contacts

To determine whether purity could be achieved by stagewise extraction, a series of contacts (10) of the loaded solvent with fresh feed were carried out. After 10 contacts with a feed containing 0.21 g Th/L, the loaded solvent contained 2.04 g Th/L and 0.006 g Fe/L or a Th/Fe ratio of 340.

Thus, a combination of extraction time, number of stages, and use of scrubbing can upgrade the thorium purity.

Stripping

a) Strip Isotherm

Stripping isotherms, using 1.5 and 3.0 M HNO_3 were constructed by varying the phase ratios and contacting the strip acid with a 4% Primene JMT (0.1 M) loaded solvent. Although the equilibrium isotherm for the 3.0 M HNO_3 appears to be the best in order to obtain minimum stage requirements, the 1.5 M HNO_3 would probably be more practical to use in the plant. A strip solution containing 28 g Th/L can be attained with the 3.0 M HNO_3 strip solution and 23 g Th/L with the 1.5 M HNO_3 strip solution. The strip isotherms are shown in Fig. 2. In Fig. 3 is shown the McCabe Thiele diagram for the 1.5 M HNO_3 strip indicating two stages to obtain a solvent containing less than 0.019 Th/L. However a single stage stripping, to obtain 0.1 g Th/L, may be sufficient.

b) Kinetics of Stripping

Kinetic stripping tests using 1.5 M HNO_3 indicated that 2-3 minutes would be required to obtain maximum stripping in one stage. However, at

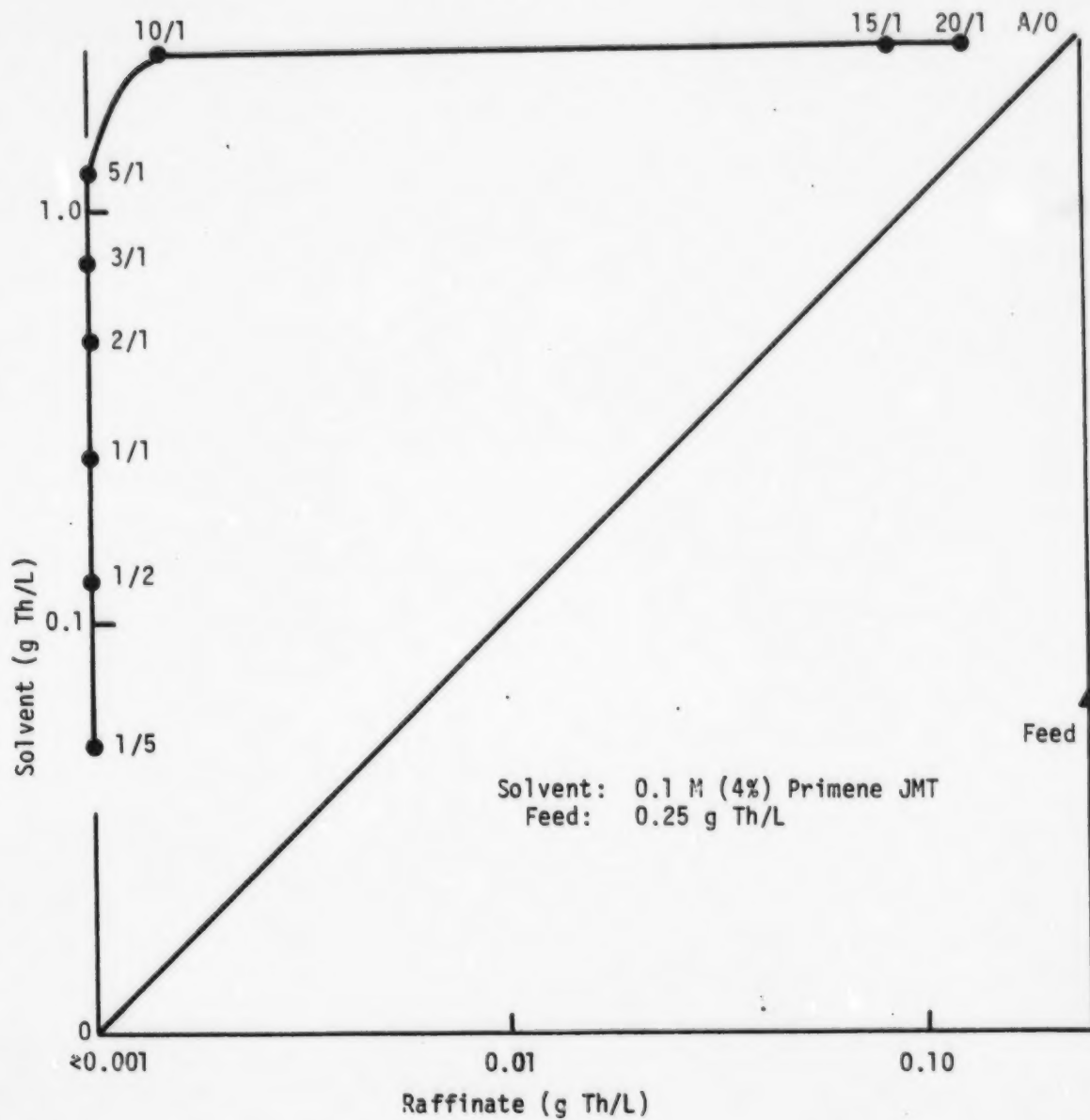


Fig. 1 Equilibrium Diagram for Extraction of Thorium With Primene JMT

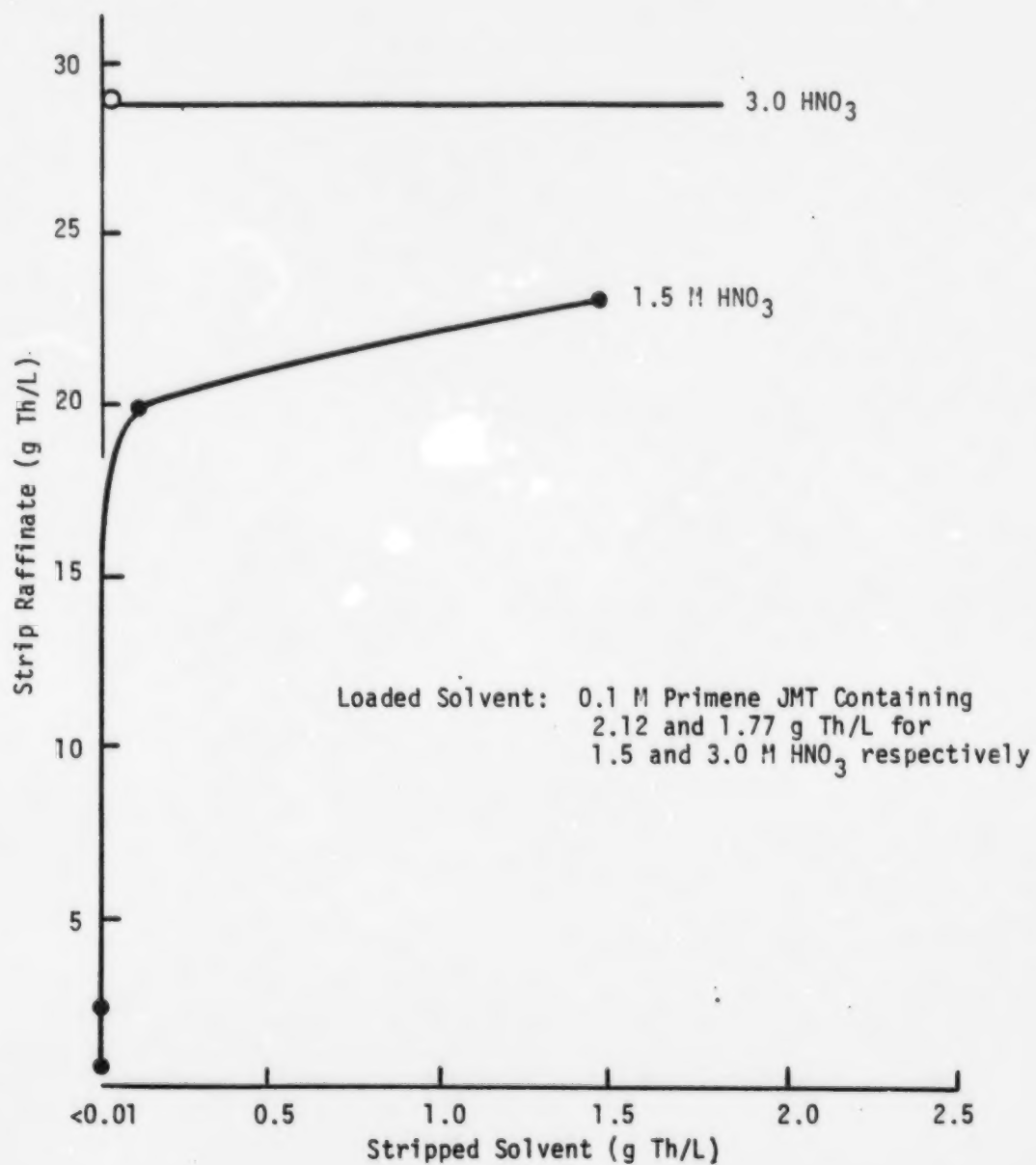


Fig. 2 Equilibrium Isotherms for Stripping Th from Primene

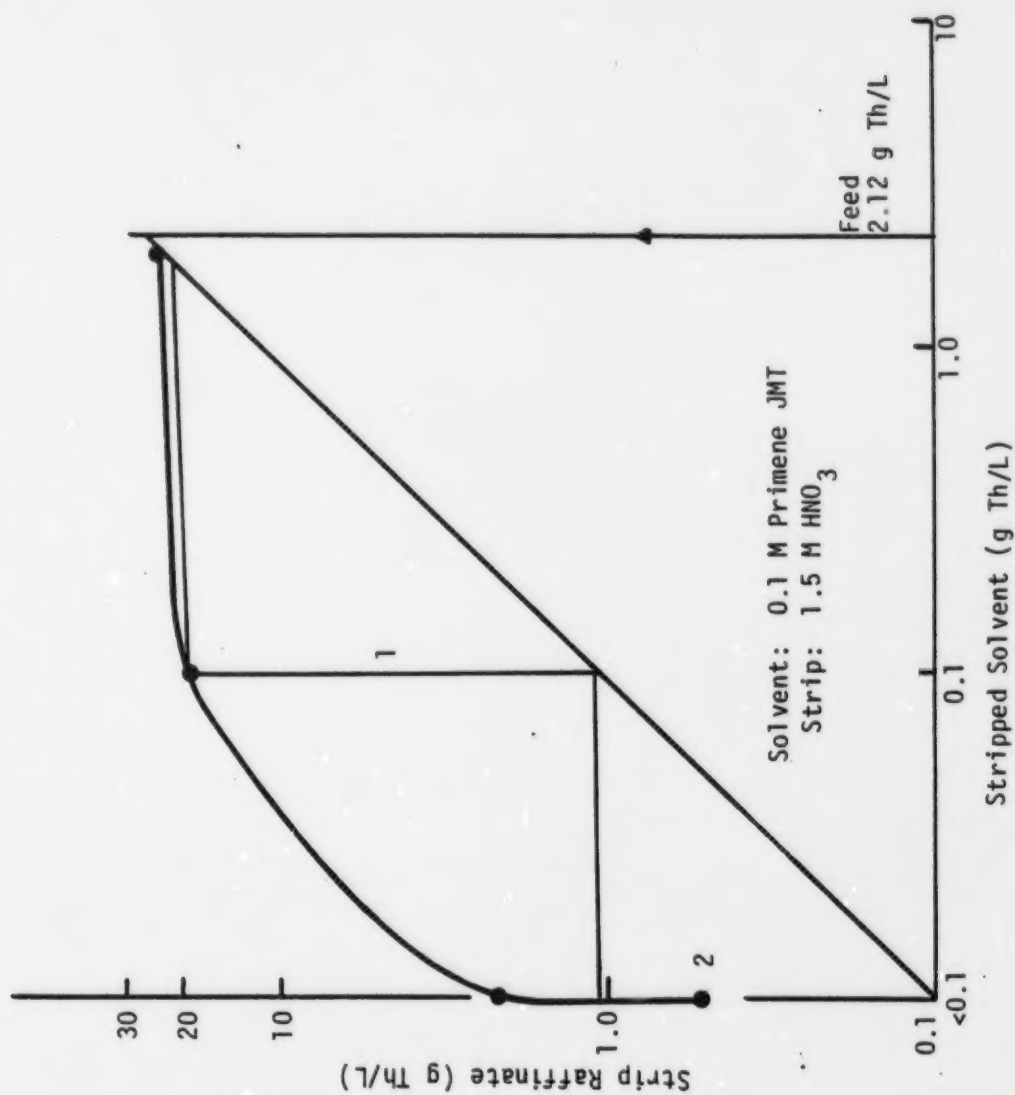


Fig. 3 McCabe-Thiele Stripping Diagram Using 1.5 M HNO_3

shorter times, where perhaps 60% Th was stripped, the Th/Fe discrimination was 80, compared to a value of about 52 at 1 minute and 34 at 3 minutes. The tests were at an O/A ratio of 10/1, using 1.5 M HNO_3 strip solution, and the time was varied over the range 10 seconds to 300 seconds. The data are shown in Fig. 4.

TBP Circuit

Following the extraction from the ion exchange barren liquor, and stripping with HNO_3 , the conceptual flowsheet on which the present work is being conducted would employ a second extraction circuit using TBP to further purify the thorium.

a) Effect of TBP Concentration and HNO_3 Concentration

A series of tests were performed to determine if there was an optimum HNO_3 concentration that would be amenable to TBP extraction, as well as to determine the optimum TBP concentration. Thus the HNO_3 concentration would have to relate to the HNO_3 concentration used in the Primene stripping circuit. These tests were on a synthetic strip HNO_3 solution containing, in g/L, 19.9 Th, 0.94 U and 1.15 Fe where the nitric acid concentration was varied at 0.5, 1.0 and 1.5 M HNO_3 and the solvent was 25, 50 and 75% TBP in Shell 140 kerosene. The phase ratio was 1 for the 5 minute contact time.

The results are summarized in Table 1, Fig. 5 and Fig. 6 indicating a 50% TBP concentration appears suitable and that a 1.5 M HNO_3 results in the best discrimination of Th over Fe and U. The difference between using a 50% or 75% solvent didn't appear to be large enough considering the small difference in extraction results, so the lower concentration TBP was used in subsequent tests.

b) Use of a Mixed HNO_3 + H_2SO_4 Feed to TBP Extraction

A few tests were carried out to determine whether a mixed strip of the amine circuit would provide for a better extraction upon subsequent contact with TBP. A range of HNO_3 and H_2SO_4 mixtures containing 20 g Th/L, 1.09 U/L and 1.0 g Fe/L were contacted with 50% TBP at 1/1 phase ratio for 5 minutes. With excessive amounts of H_2SO_4 present the feed became turbid, indicating that precipitation of thorium was occurring. The results in Table 2 on one stable acid mixture provided clear solutions and no physical problems. However, with the addition of H_2SO_4 to the HNO_3 strip liquor the

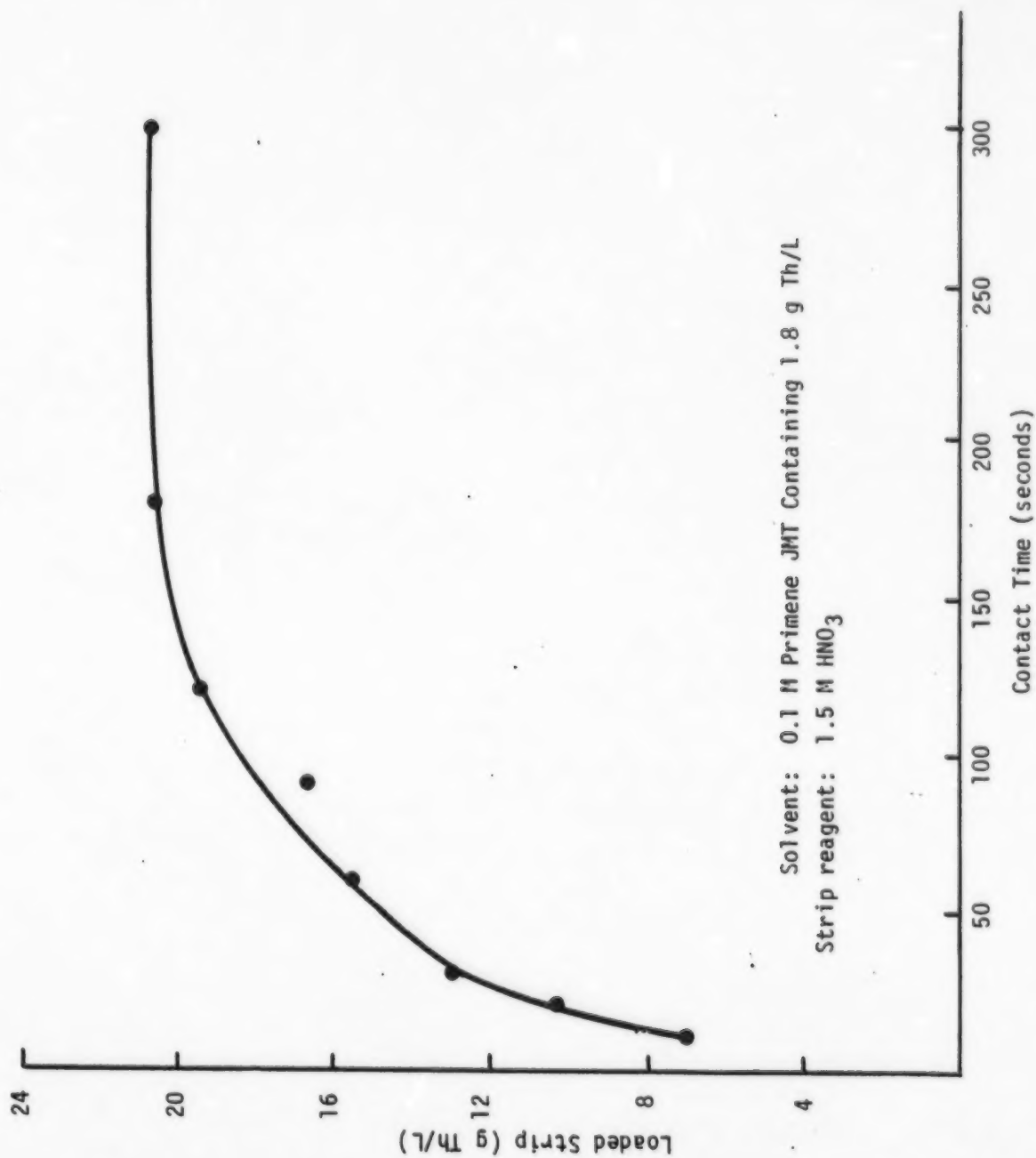


Fig. 4 Stripping Kinetic Data for 1.5 M HNO₃ - Primene JMT System

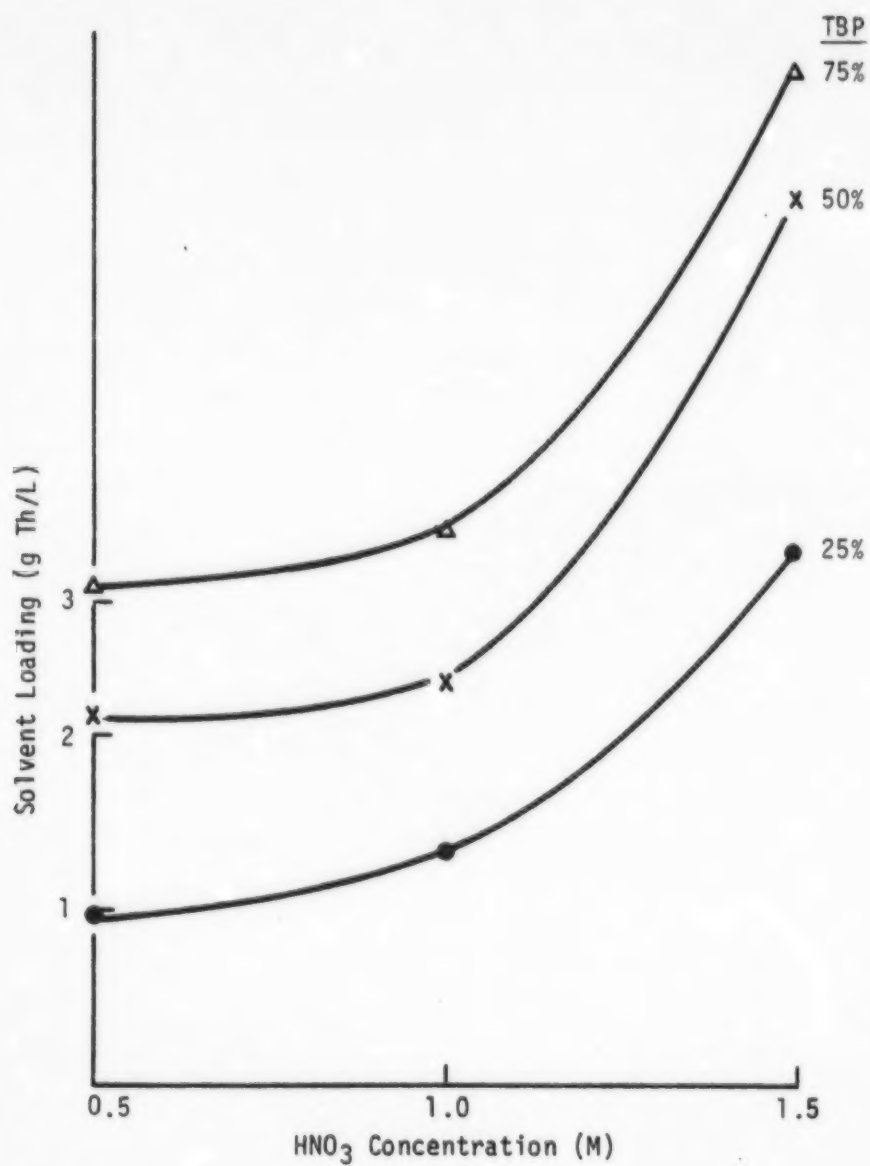


Fig. 5 Effect of TBP and HNO₃ Concentrations on Th Loading

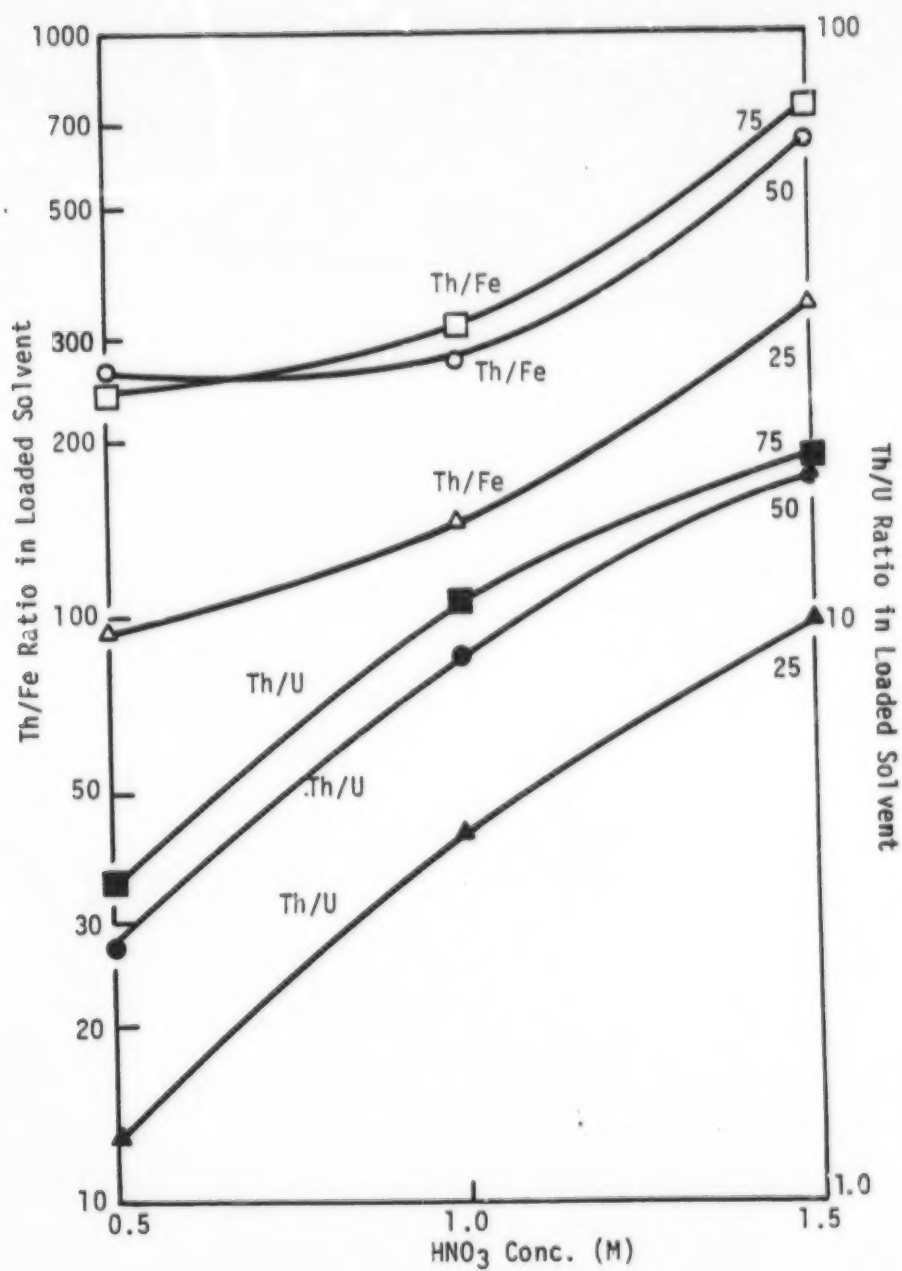


Fig. 6 Effect of TBP and HNO_3 Concentrations on Selectivity of Th/Fe and Th/U

discrimination over iron was dramatically decreased while true for thorium over uranium. No further work will be such a mixed acid system.

Table 1. Effect of TBP Concentration and HNO_3 on Thorium Extraction and Selectivity over Iron

HNO_3 (M)	TBP Concentration (%)	Solvent Loading (g Th/L)
0.5	25	0.97
	50	2.10
	75	2.83
1.0	25	1.32
	50	2.30
	75	3.15
1.5	25	3.05
	50	5.04
	75	5.78

Table 2. Mixed HNO_3 + H_2SO_4 Feed to TBP Extraction

Acid Mixture (M)		Loaded Solvent Th	Th
HNO_3	H_2SO_4		
1.5	0	5.04	6
1.5	0.5	8.90	7

c) Extraction Isotherms, 50% TBP from 1.5 or 3.0 M HNO_3

Data were collected for construction of an equilibrium extraction with 50% TBP from 1.5 M HNO_3 feed solution. synthetic solution containing, in g/L, 19.9 Th, 0.57 U were at varying phase ratios, for a contact of 5 minutes. Fig. 7 indicate that a residual amount of 4.5 g Th/L remained in the feed solution and that 5 stages would be required, resulting in a solvent of about 28 g Th/L on the 50% TBP solvent.

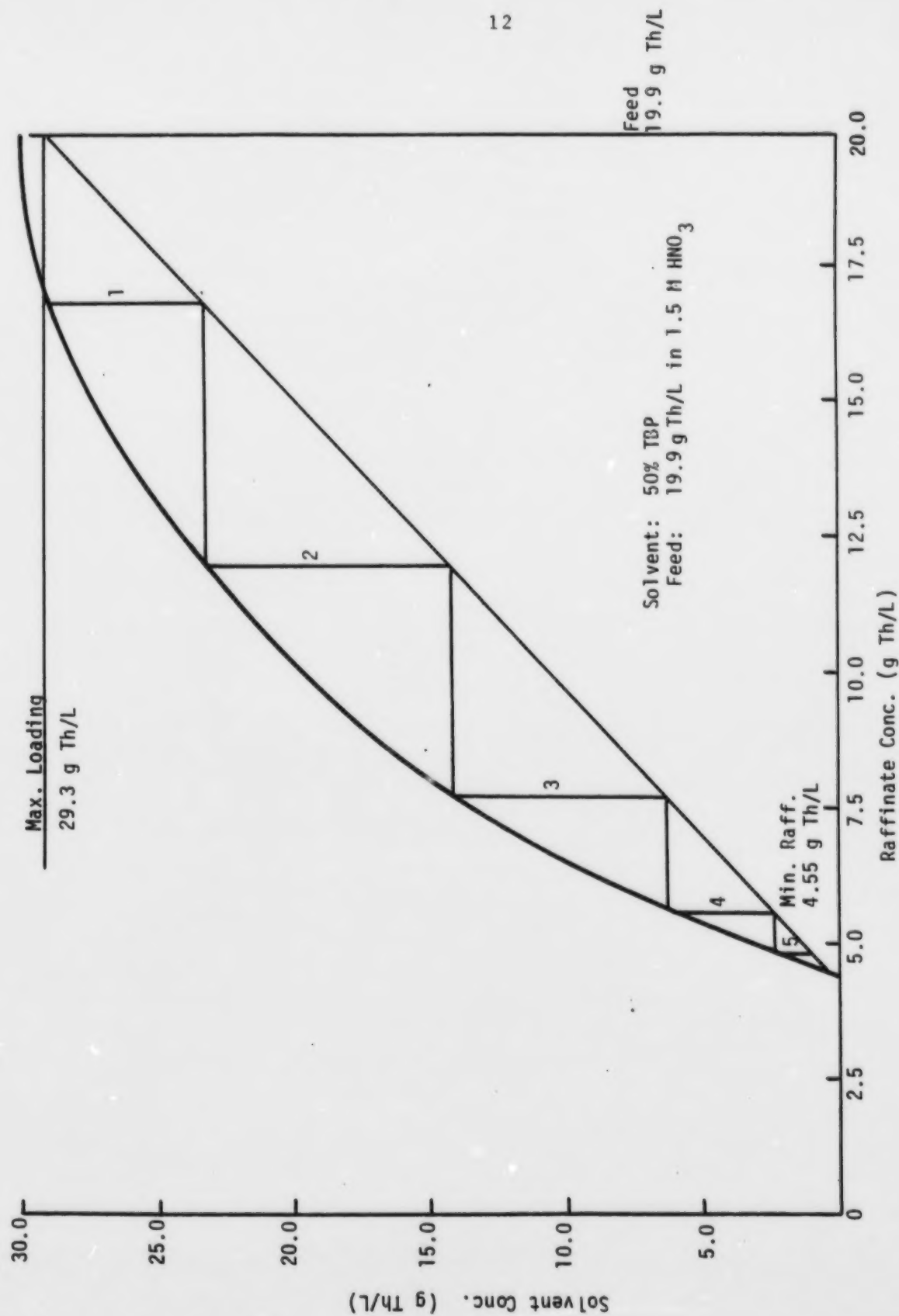


Fig. 7 McCabe-Thiele Diagram for TBP Extraction from 1.5 M HNO₃

d) Kinetics of Extraction into TBP

Kinetic tests on extraction from a feed containing 11.3 g Th/L, 0.36 g Fe/L, and 0.073 g U/L in contact with 50% TBP over a time period of 10-300 seconds indicated a minimum of 30 seconds contact was necessary.

e) Stripping

Screening tests were carried out on various possible strip reagents to determine completeness of stripping as well as the possibility of selectivity of stripping. All tests were at a phase ratio of 1 on a loaded solvent. The loaded solvent for the stripping tests contained, in g/L, 15.0 Th, 0.13 U, 0.086 Fe. The results are given in Table 3, and indicate that water appears to be economically the best strip solution for the removal of thorium from the TBP as $\text{Th}(\text{NO}_3)_4$. A stripping isotherm using water to strip 26.89 Th/L from the solvent is shown in Fig. 8 indicating 2 stages would be sufficient.

Kinetic stripping tests with water over a time period of 10 seconds to 300 seconds showed complete thorium recovery over the range tested. There was no difference in selectivity over Fe and U with time of contact.

Table 3. Stripping Th from 50% TBP - screening tests

Stripping Solution	Th		U		Fe		Selectivity	
	% Stripped	Strip(g/L)	Strip(g/L)	Strip(g/L)	Strip(g/L)	Th/Fe	Th/U	
water	70	11.4	0.063		0.0008	14,250	181	
1.0 M NH ₄ NO ₃	95	14.3	0.37		0.0008	17,875	38	
1.0 M Na ₂ CO ₃	100	15.4	0.38		0.0008	19,250	40	
1.0 M (NH ₄) ₂ CO ₃	100	15.7	0.49		0.0003	52,333	32	

Continuous Testing in Mixer Settler Circuit

Continuous countercurrent testing in a small mixer settler unit was carried out to verify the bench data as regards stages and conditions. The initial test for 4 hours was to determine the extraction of thorium from the ion exchange barren solution into 0.1 M (4%) Primene JMT. The solvent also contained 5% isodecanol in Varsol 140 diluent. Prior to extraction the solvent was pre-equilibrated with 5% H_2SO_4 , O/A 5/1. The 2-stage extraction circuit was run at an A/O ratio 10/1, flows of 400/40 mL/min. (The bench data McCabe-Thiele suggested a single stage would be sufficient.)

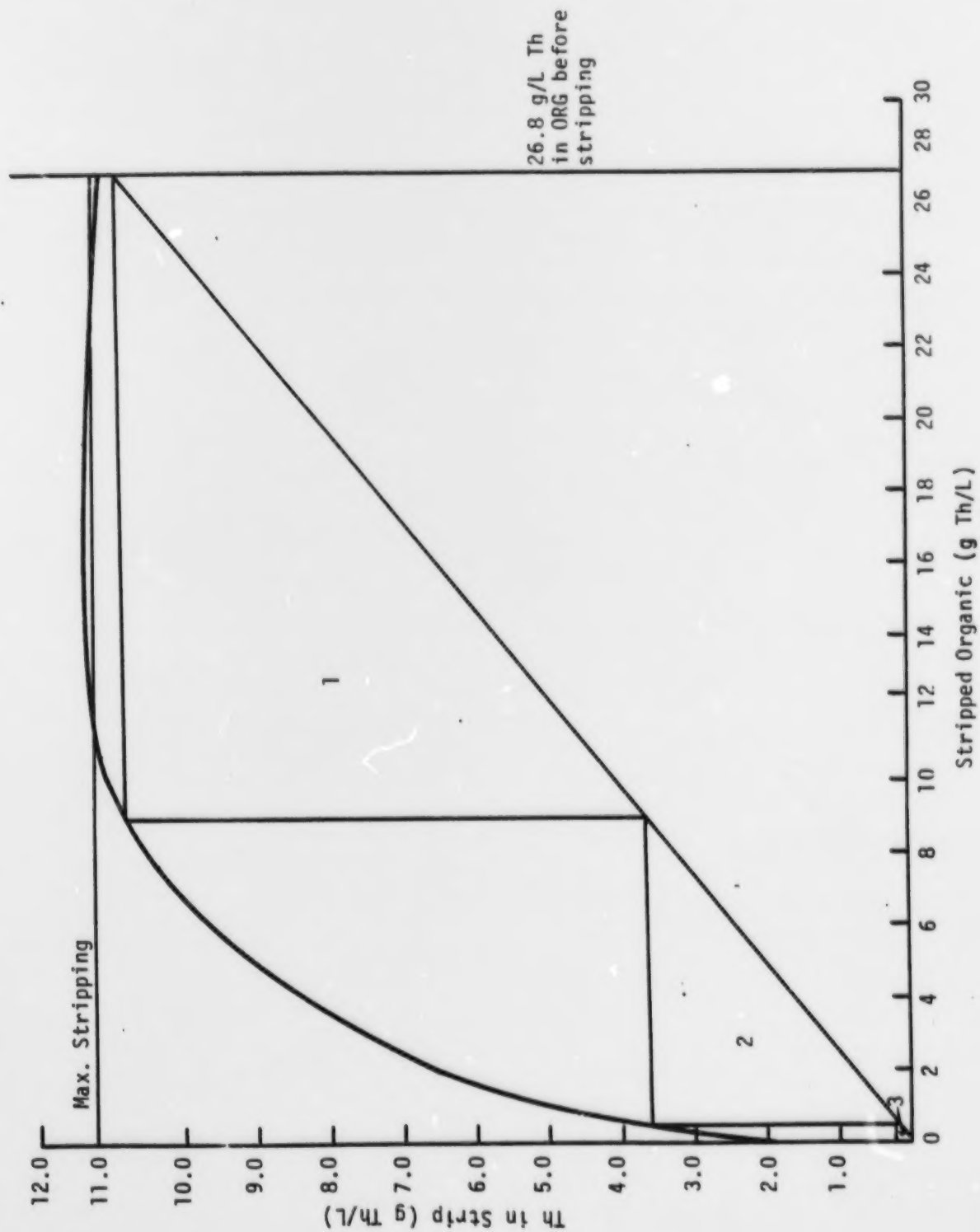


Fig. 8 Stripping Isotherm of Th With Water From 50% TRP

The feed solution contained 0.24 g Th/L, 0.013 g U/L and 1.93 g Fe/L. Steady state was not quite reached after 4 hours, but the raffinate was reduced to 0.001 g Th/L with the loaded organic containing 1.99 g Th/L, 0.21 g Fe/L and 0.013 g γ /L. The strip circuit was run at O/A 10/1, flow 280/28 mL/min. A subsequent test with A/O 400/40 mL/min indicated that steady state was complete after 16 hours. In that run, after 20 hours, the loaded solvent contained 2.86 g Th/L and 0.01 g U/L. Loaded solvent was collected to run a stripping circuit. The 2-stage stripping circuit, using 1.5 M HNO_3 was operated at O/A 10/1 for about 1 hour which was insufficient to obtain steady state. The strip liquor contained 7.51 g Th/L, 0.24 g U/L and 0.001 g Fe/L. Thus the discrimination over iron and uranium was Th/Fe 7240 and Th/U 31. The retention time in each stage of extraction was 3.16 minutes while in the stripping circuit the time was 4.73 minutes.

DISCUSSION AND CONCLUSIONS

The research to date has indicated that possibly a double extraction system may be employed to treat the barren liquors from uranium processing. The first circuit would consist of a 2-stage extraction with Primene JMT followed by 2-stage stripping with 1.5 M HNO_3 . Although no continuous testing has yet been carried out on the second circuit, where 50% TBP would contact the 1.5 M HNO_3 strip solution containing the thorium, no problems are anticipated in the 5 extraction and 2 strip stages.

Further bench tests on the possibility of using a scrub stage in each circuit may be required. One of the important aspects in the next phase of the investigation is to produce a sufficiently large quantity of the loaded amine so that the subsequent evaluation in the TBP circuit can be meaningful. Also the work must produce sufficient final products for chemical analyses and evaluation as a thorium feed for AECL. Therefore there is the possibility that a pilot plant will have to be run at one of the mills in Elliot Lake in order to provide sufficient material.

Precipitation tests will also be performed on strip liquors from both circuits in order to compare the relative purity of the products.

The conceptual flowsheet, as a result of the present data, is shown in Fig. 9.

ION EXCHANGE BARREN URANIUM SOLUTION
0.24 g Th/L

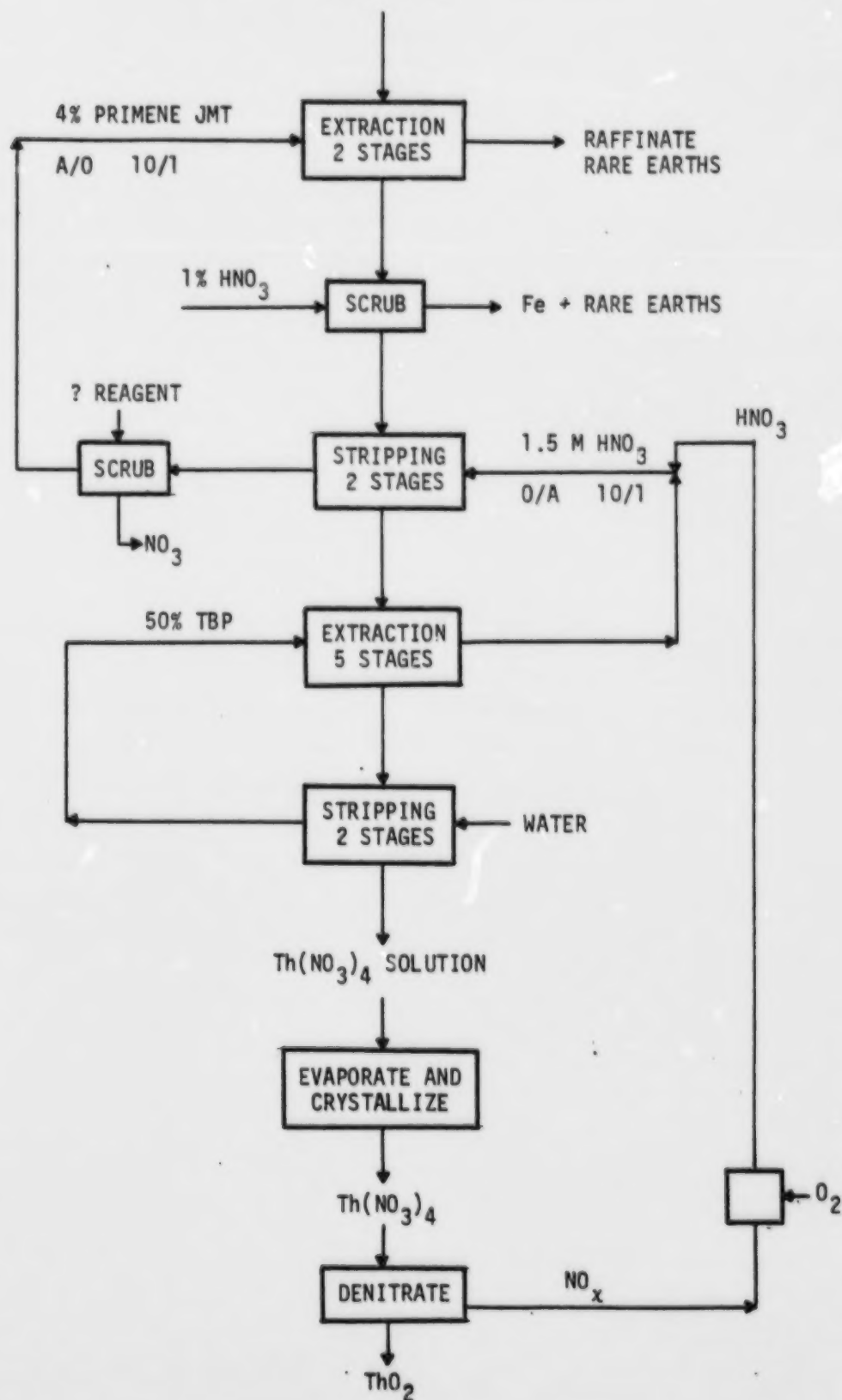


Fig. 9 Schematic of Conceptual Flowsheet

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